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A STUDY ON THE REACTION BETWEEN CO_2 AND ALKANOLAMINES IN AQUEOUS SOLUTIONS

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Abstract—Literature data on the rates of reaction between CO_2 and alkanolamines (MEA, DEA, DIPA, TEA and MDEA) in aqueous solution are discussed. These data induced us to carry out absorption experiments of CO_2 into aqueous DEA, DIPA, TEA and MDEA solutions from which the respective rate constants were derived. The experimental technique was similar to that used by Laddha and Danckwerts[30].

The results for DEA and DIPA were analysed by means of a zwitterion-mechanism which was derived from the mechanism originally proposed by Danckwerts[16], and were found to fit the model extremely well.

The reaction rate of CO_2 with aqueous TEA and MDEA solutions shows a significant base catalysis effect which is also reported by Donaldson and Nguyen[17] and Barth *et al.*[4]. The results for TEA correspond very well with those of Donaldson and Nguyen[17] and Barth *et al.*[4].

INTRODUCTION

In the last decades, alkanolamines have acquired a well-established position in gas-treating for the removal of the acidic components H_2S and CO_2. Industrially important alkanolamines are: mono-ethanolamine (MEA), di-ethanolamine (DEA), di-isopropanolamine (DIPA) and methyl-di-ethanolamine (MDEA)[27]. In general these amines are used in aqueous solutions, but for particular applications combined solvents are more suited (e.g. water and sulfolane in the Shell "Sulfinol" process)[27].

Due to the high and still sharply rising energy cost involved in the operation of gas-treating plants, the incentive for development of (even slightly) more efficient processes is considerable.

Nowadays large savings in operation and capital cost are obtained by the selective removal of H_2S from CO_2 containing gases, not only in situations where H_2S is the only component to be removed. Even in LNG production, where the CO_2 has to be removed to around 100 ppm so as to avoid plugging of the cryogenic equipment, selective H_2S absorption is economically very attractive, using sophisticated treating schemes as described by McEwan and Marmin[33]. Increasing the selectivity reduces the solvent circulation rate and therefore the steam consumption in the regenerators and, moreover, reduces the dimensions of sulphur recovery and tail-gas units.

The H_2S selectivity in these treating processes depends largely on 3 factors: (1) the kinetics of the reactions between H_2S/CO_2 and alkanolamine solutions; (2) the mass transfer properties of the absorption equipment; (3) the equilibria in H_2S–CO_2–amine systems. In this work we focused our attention on the first factor.

As the reaction between H_2S and aqueous alkanolamines involves only a proton transfer, this reversible reaction can be considered to be infinitely fast[15] and hence the absorption rate is entirely mass transfer controlled under practical conditions[36].

The reactions between CO_2 and alkanolamine solutions, however, proceed at a finite rate, different for the various amines[15, 47]. From a purely kinetic point of view the selectivity for H_2S therefore only depends on the CO_2 reaction rate. Consequently this work deals with the reaction of CO_2 and aqueous alkanolamine solutions.

Until recently the mechanism and kinetics for this reaction were considered to be simple and straightforward[15] for all alkanolamines, although large discrepancies in data have been reported for DEA[1, 17, 18, 19, 22, 26, 43, 47] and TEA[17, 19, 25, 26, 43]. Danckwerts proposed a comprehensive reaction mechanism[16] which is essentially able to cover all kinetic data for both primary and secondary alkanolamines. In addition, Laddha and Danckwerts[30] published experimental results for aqueous MEA and DEA, which seem to support the proposed mechanism.

For tertiary alkanolamines Donaldson and Nguyen[17] suggested a base catalysis of the CO_2 hydratation reaction.

In this study we attempt to critically summarize available kinetic data for MEA, DEA, DIPA, TEA and MDEA and present new data on DEA, DIPA, TEA and MDEA.

REVIEW OF LITERATURE KINETIC DATA

General remarks

Comparison of literature data on kinetics of CO_2–alkanolamine reactions is a complicated matter, because the authors use different experimental techniques, physico-chemical data and amine purities. The latter factor is usually overlooked, but even very small amounts of primary amine contaminants in secondary amines and

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primary and secondary amines in tertiary amines can enhance the absorption rate drastically. A mathematical approach for the estimation of the effect of these contaminants is given by, e.g. Jhaveri[23] and Onda *et al.*[35], but correction of published kinetics remains ineffective due to lack of data on amine purities.

In order to verify the conditions for pseudo first order absorption experiments and—what is more important—to obtain reaction rate constants from these experiments, the physico-chemical parameter $m_{CO_2} \cdot \sqrt{D_{CO_2}}$ is needed. In literature, the value of this parameter is derived in various ways, as will be demonstrated further, and this may lead to discrepancies in the rate constants calculated from absorption experiments.

As CO_2 reacts with aqueous alkanolamines, it is not possible to measure m_{CO_2} or D_{CO_2} in these solutions directly. This problem is usually overcome by measuring these parameters with the non-reacting N_2O which is almost identical[1, 12, 29]. Laddha *et al.*[29] and Laddha and Danckwerts[30] made it plausible that the CO_2 parameters can be obtained from N_2O measurements by the relation:

$$m_{CO_2} \cdot \sqrt{D_{CO_2}} = 1.43 * m_{N_2O} \cdot \sqrt{D_{N_2O}}. \quad (1)$$

Very often the diffusivity, D_{N_2O} or D_{CO_2}, is correlated to the viscosity of the solution at a constant temperature by [40]:

$$D \cdot \eta^n = \text{constant} \quad (2)$$

where usually $0.5 < n < 1$.

Sada *et al.* have determined m_{N_2O}, D_{N_2O} and η for aqueous MEA[41], DEA[45, 46], DIPA[46] and TEA[45, 46] solutions. In Fig. 1 $\ln[(D_{N_2O\text{-amine}})/(D_{N_2O\text{-water}})]$ is plotted vs $\ln[\eta_{amine}/\eta_{water}]$ and according to eqn (2) this should yield a straight line through the origin with slope n. For all amines, however, the fit is very poor and, moreover, n depends on the type of amine (e.g. DEA: $n = \sim 0.3$, DIPA: $n = \sim 0.7$). Therefore, the use of eqn (2) for correlation of diffusivity data in (aqueous) alkanolamine solutions is not recommended, as was already pointed out by Laddha and Danckwerts[30].

The Stokes–Einstein equation, in fact a special case of eqn (2) where $n = 1$, is used by a number of authors for the estimation of diffusivities[18, 20, 47]. This equation grossly overestimates the dependence on the solution viscosity. For this reason Hikita *et al.*[20] calculate from their absorption experiments a "salting-in" effect for the CO_2-solubility in MEA. Most of the data measured, however, unambiguously show a "salting-out" effect[12, 29, 41, 45, 46].

Another approach used by several authors, is to employ the CO_2 solubility in water for the interpretation of their experiments[1, 18, 47]. Because obviously m_{CO_2} and D_{CO_2} cannot be correlated separately, in a satisfactory way, we preferred to use the combined parameter $m_{CO_2} \cdot \sqrt{D_{CO_2}}$ as obtained from N_2O experiments for the interpretation of literature data and our own data measured at 25°C. The values of $m_{CO_2} \cdot \sqrt{D_{CO_2}}$ are calculated from literature for MEA[12, 30, 41], DEA[30, 45, 46], TEA[45, 46] and DIPA[46], by interpolating the solubilities. These data are complemented by our measurements for DIPA and MDEA (see Table 1). The experimental technique is described elsewhere[8, 9]. All data are summarized in Fig. 2 and polynomial fittings are given in Table 2. These correlations are used throughout this work.

With respect to the reaction rate dependence on the CO_2 concentration, invariably a first order rate equation

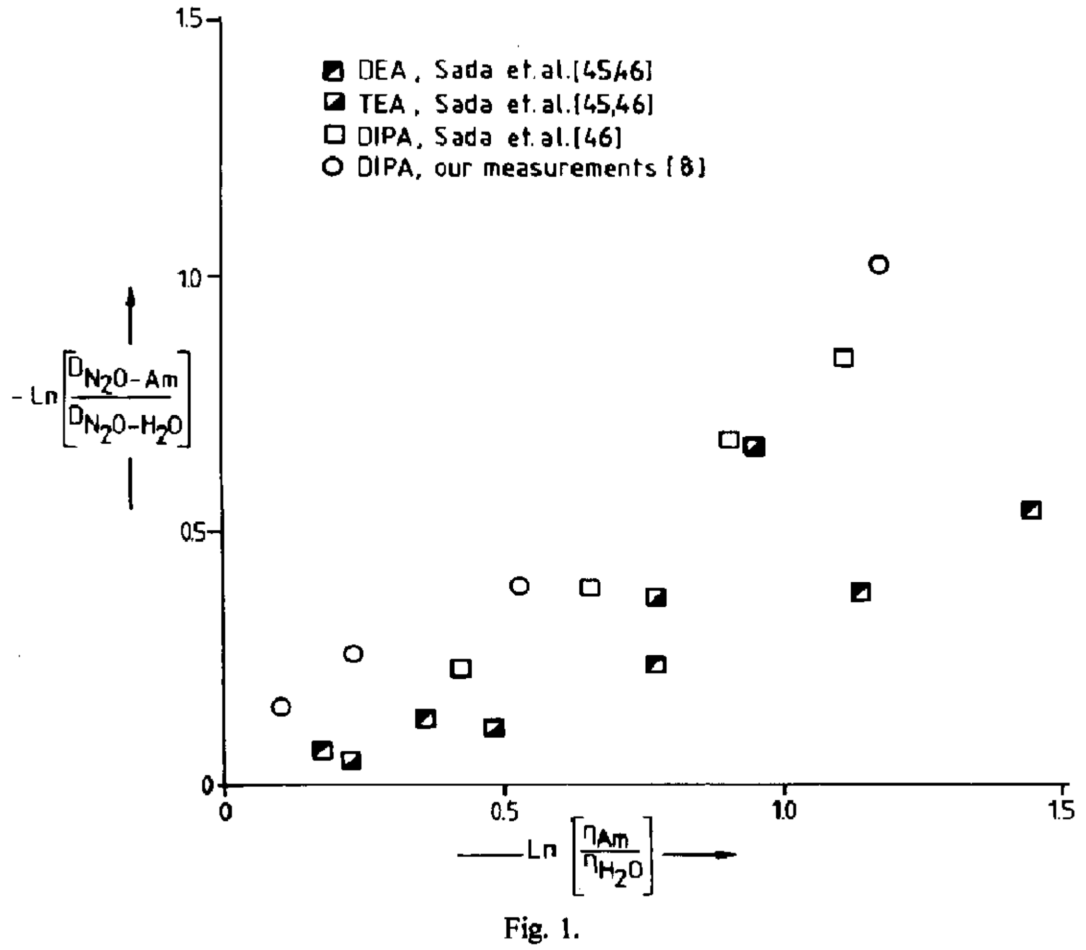


Fig. 1.

Table 1. $m_{N_2O}\sqrt{D_{N_2O}}$ as a function of [Am] for DIPA and MDEA at 25°C[8]

Amine	[Am] mole/l	$m_{N_2O}\sqrt{D_{N_2O}}$ * 10^5 m/s$^{1/2}$
DIPA	0.580	2.15
	1.280	1.67
	1.753	1.31
	2.330	1.03
MDEA	0.511	2.23
	1.060	2.05
	1.440	1.78
	2.056	1.65

is found in literature. In the following we shall, therefore, consider the influence of the amine concentration only.

MEA

Literature sources with kinetic data on aqueous MEA are summarized in Table 3. Wherever possible and necessary, the reaction rate constants at 25°C have been corrected to the standard data for $m_{CO_2}\cdot\sqrt{D_{CO_2}}$ by using the equations of Table 2. Without any exception a first order reaction rate in MEA has been found regardless experimental techniques and conditions. The data show fairly good agreement as can be concluded from an Arrhenius plot (Fig. 3). Danckwerts and Sharma's[15] rate constants at 18 and 35°C seem to be fairly high, probably due to the use of too low values of $m_{CO_2}\cdot\sqrt{D_{CO_2}}$ calculated by the Stokes–Einstein equation. The reason of the relatively large scatter in data at 25°C is not quite clear, but could be attributed to the different experimental techniques.

The data most recently published, i.e. those of Laddha and Danckwerts[30], Donaldson and Nguyen[17] and Alvarez-Fuster *et al.*[1], fit the equation by Hikita *et al.*[19]:

$$\log_{10} k_2 = 10.99 - 2152/T \text{ (1./mole.sec)} \quad (3)$$

extremely well. We concluded therefore that these literature sources provide the reaction rate constant of the CO_2–MEA reaction with good accuracy and that no additional kinetic data on MEA seem to be required.

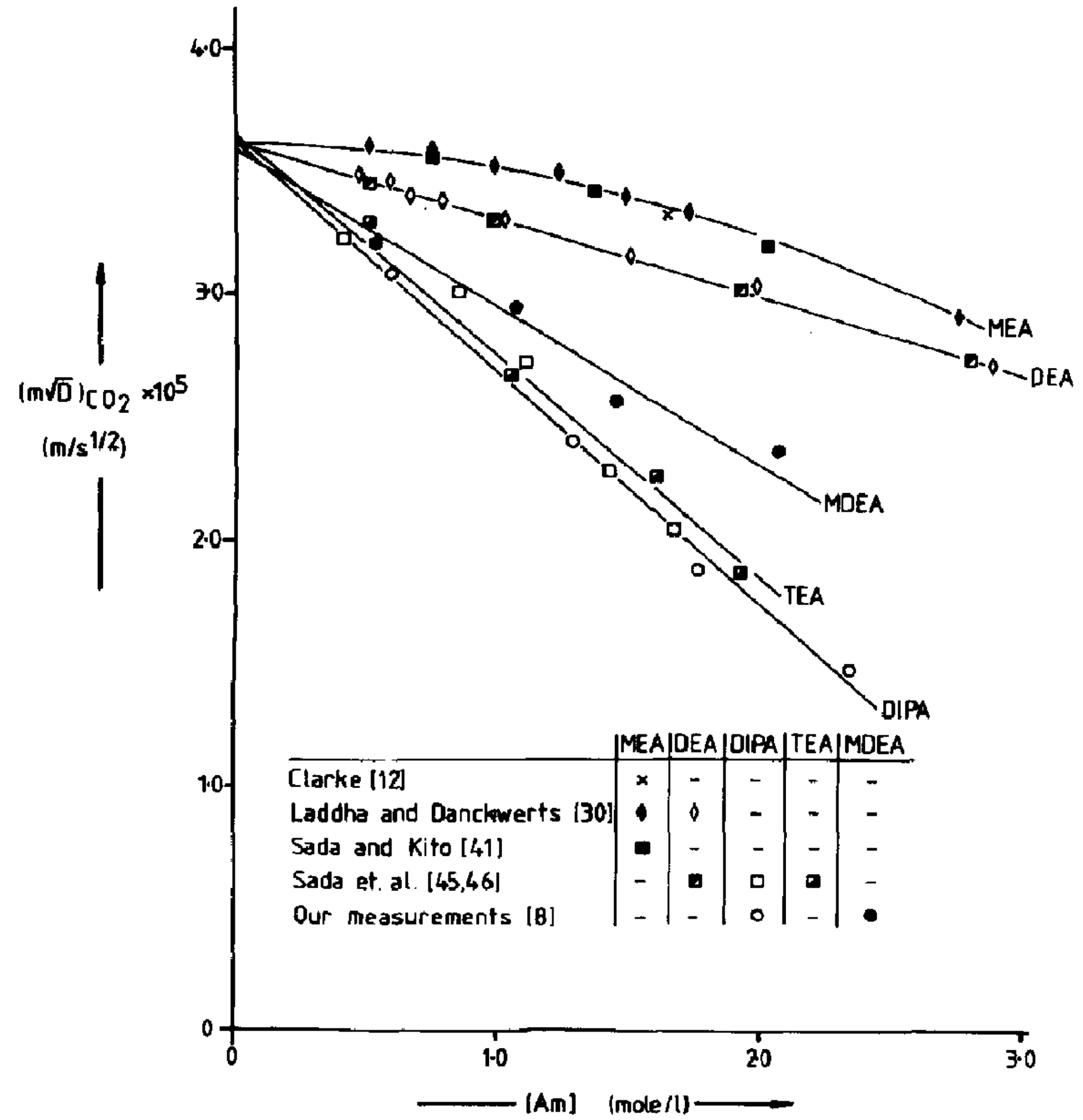


Fig. 2.

Table 2. Correlations used for the calculation of $m_{CO_2}\sqrt{D_{CO_2}}$ as a function of [Am]

Amine	Reference	Correlation	average deviation
MEA	[12, 30, 41]	$m_{CO_2}\sqrt{D_{CO_2}} = 3.61*10^{-5}-1.87*10^{-7}$ [Am] $-8.73*10^{-7}$[Am]^2 (m/s$^{1/2}$)	0.52%
DEA	[30, 45, 46]	$m_{CO_2}\sqrt{D_{CO_2}} = 3.61*10^{-5}-3.10*10^{-6}$[Am] (m/s$^{1/2}$)	0.40%
DIPA	[8, 46]	$m_{CO_2}\sqrt{D_{CO_2}} = 3.63*10^{-5}-9.48*10^{-6}$[Am] (m/s$^{1/2}$)	2.5%
TEA	[45, 46]	$m_{CO_2}\sqrt{D_{CO_2}} = 3.65*10^{-5}-9.11*10^{-6}$[Am] (m/s$^{1/2}$)	2.1%
MDEA	[8]	$m_{CO_2}\sqrt{D_{CO_2}} = 3.53*10^{-5}-6.03*10^{-6}$[Am] (m/s$^{1/2}$)	2.2%

Table 3. Literature data on the reaction between CO_2 and aqueous MEA

reference	temperature (range) °C	[MEA] mole/l	k_2 l/mole.s	E_{act} kJ/mole	Experimental technique
Hikita et.al.[19]	5.6 - 35.4	0,0152-0.177	log k_2 = 10.99-2152/T	41.2	Rapid mixing method
Jensen et.al.[22]	18	0.1, 0.2	4065 [14]	-	Competition method with 0.1 and 0.2 M NaOH
Danckwerts and Sharma [15] Sharma [47]	18	1.0	5100	41.8	Laminar jet
Alvarez-Fuster et. al. [1]	20	0.2 - 2.02	4300	-	Wetted wall column
Astarita [3]	21.5	0.25 - 2.0	5400	-	Laminar jet
Clarke [12]	25	1.6, 3.2, 4.8	7500	-	Laminar jet
Donaldson and Nguyen [17]	25	0.0265-0.0828	6000	-	Facilitated transport in aqueous amine membranes
Groothuis [18]	25	2.0	6500 5720*	-	Stirred cell
Laddha and Danckwerts [30]	25	0.49 - 1.71	5720	-	Stirred cell
Sada et.al.[42]	25	0.245-1.905	8400	-	Laminar jet
Sada et.al.[44]	25	~0.2 - 1.9	7140	-	Laminar jet
Sharma [47] Danckwerts and Sharma [15]	25	1.0	7600 6970*	41.8	Laminar jet
Sharma [47] Danckwerts and Sharma [15]	35	1.0	9700 [43] 13000 [13]	41.8	Laminar jet
Leder [32]	80	-	$9.4 * 10^4$	39.7	Stirred cell

* corrected for $m_{CO_2}\sqrt{D_{CO_2}}$ in table 2.

DEA

The kinetic data of the CO_2–DEA reaction are given in Table 4. The reaction rate expressions found in literature, vary widely in dependence on the DEA and OH^- concentrations. As pointed out by Danckwerts[16], the principal reason for this disagreement is the fact that the reaction mechanism is far more complicated than most authors assumed. With respect to this point we deemed it useful to provide additional data on the CO_2–DEA reaction over a wide range of conditions.

DIPA

Only two investigations on reaction rates of CO_2 with DIPA have been published in open literature (see Table

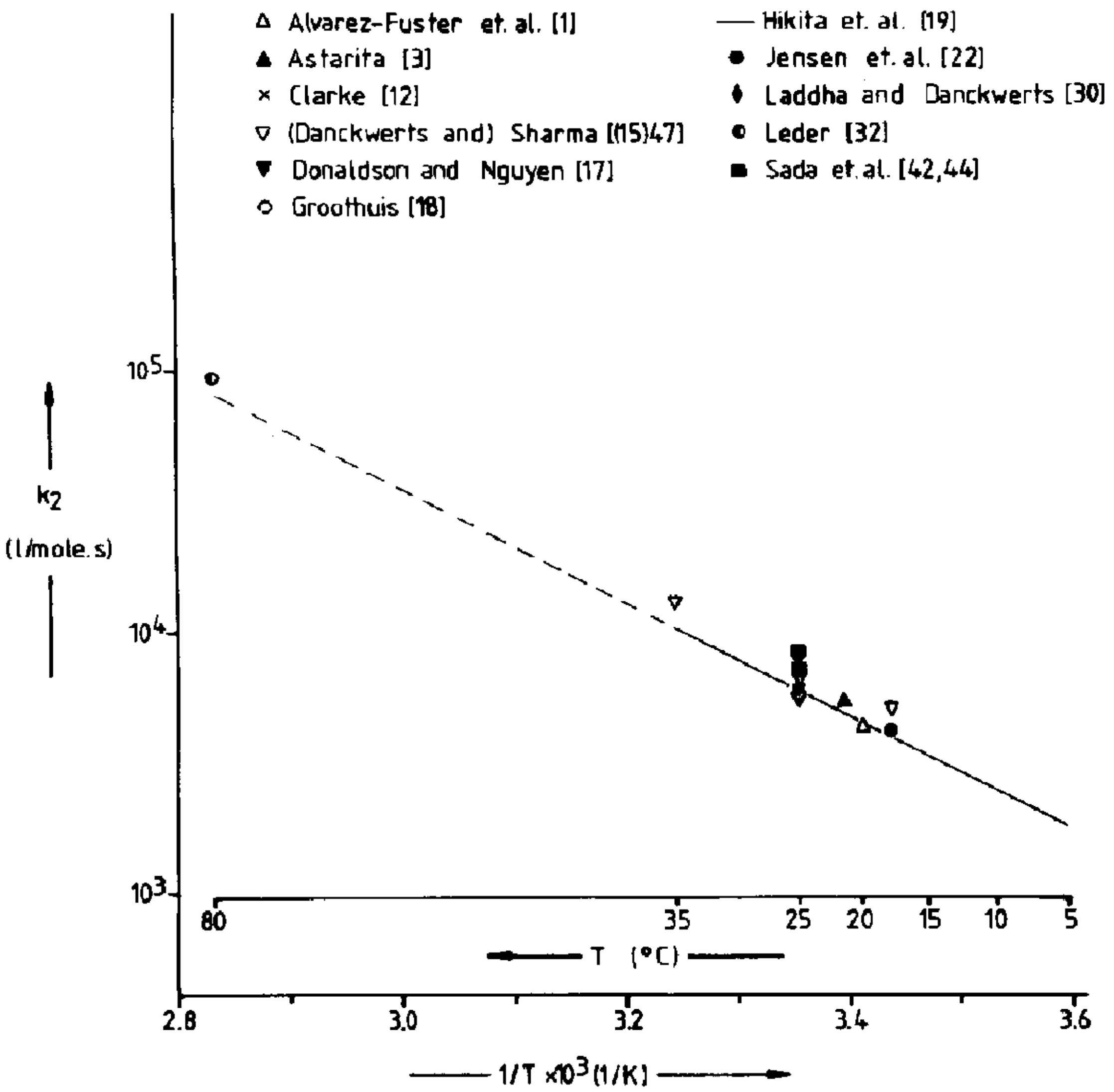


Fig. 3.

5). As both authors did not vary the amine concentrations during their experiments, it is questionable whether the reaction rate really is first order in amine. Moreover, as the molecular structure of DIPA is similar to that of DEA, the reaction mechanism is likely to be complicated, as is the case for DEA. Therefore we included DIPA in our kinetics measurement programme.

TEA

The rate constants for the CO_2–aqueous TEA solutions show in general a first order dependence on the TEA-concentrations (see Table 6). The results of Jørgensen and Faurholt[25] and Jørgensen[26] at pH ~ 13, however, include a hydroxyl ion term caused by monoalkyl carbonate formation, which is not found at pH < ~11[17, 19]. The rate constants at 25°C vary from 2.8 l./mole.sec[17, 4] up to 50 l./mole.sec (Hikita *et al.*[19]). Because of these discrepancies we provide some data on the CO_2–TEA reaction.

MDEA

In the open literature only one single investigation is published which contains only little information on the reaction of CO_2 in aqueous MDEA solutions[4]. Barth *et al.*[4] also present some information on reaction mechanism and rate but they used a relatively high pK_a value in the evaluation of their experiments ($pK_a = 8{,}65$ instead of $pK_a = 8.52$ at 25°C as reported by Perrin[37]). This results in an overestimation of the contribution of the hydroxyl ions to the measured reaction rate and in a too low contribution by MDEA. Therefore we also included MDEA in our test programme.

THE REACTION MECHANISM

In aqueous solutions of primary and secondary alkanolamines, the following reactions with CO_2 occur (see e.g. [15, 16]):

carbamate formation:

$$CO_2 + 2R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (4)$$

bicarbonate formation:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (5)$$

carbonic acid formation:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \quad (6)$$

alkylcarbonate formation:

$$CO_2 + R_1R_3\underset{\substack{|\\ OH}}{C} — C — NH + OH^- \rightleftharpoons$$

$$R_1R_3 — \underset{\substack{|\\ O\\ \diagdown CO_2^-}}{C} — C — NH + H_2O \quad (7)$$

Table 4. Literature data on the reaction between CO_2 and aqueous DEA

reference	temperature (range) °C	DEA mole/l	$k_1 = \frac{r}{[CO_2]}$ s^{-1}	E_{act} $\frac{kJ}{mole}$	Experimental technique
Blanc and Demarais [5]	20–60	0.05–4.0	$10^{(\frac{-2274.5}{T} + 10.4493)} * [DEA]$	-	Wetted-wall column
Hikita et.al[19]	5.8–40.3	0.174–0.719	$10^{(12.41 - \frac{2775}{T})} * [DEA]^2$	53.1	Rapid mixing method
Van Krevelen and Hoftijzer [28]	19–56	0.05–3	$260\ [DEA]^2$	-	Packed column
Nunge and Gill [34]	29.4,35,40.6	~10 – ~12	$C*[DEA]^2$	54.4	Agitated vessel
Jørgensen [26]	0	0.1,0.2,0.3	$(730+4910*[OH^-])[DEA]$ $(692+3380[OH^-]+1056[DEA])*[DEA]$[16]	-	Competitive reaction with 0.1,0.2,0.3 M NaOH
Laddha and Danckwerts [31]	11	0.5–2.0	$\frac{[DEA]}{\frac{1}{890} + \frac{1}{560[DEA]}}$	-	Stirred cell
Jensen et.al[22]	18	0.1,0.2	$5080\ [DEA]$	-	Competitive reaction with 0.1,0.2 M NaOH
Jørgensen [26]	18	0.1,0.2,0.3	$(3990+13950[OH^-])[DEA]$	-	Competitive reaction with 0.2,0.3 M NaOH
Sharma [47]	18	1.0	$1000\ [DEA]$	~41.8	Laminar jet
Coldrey and Harris [13]	19	0.1–1.0	$430\ [DEA] + 1000[OH^-]^{\frac{1}{2}} - \frac{60([DEAH^+]+[Product])}{[DEA][CO_2]}$		Rapid mixing method with 0.002–0.005 M NaOH
Alvarez-Fuster et.al.[1]	20	0.25–0.82	$840\ [DEA]^2$	-	Wetted-wall column
Ratkovics and Horvath [39]	20	0.108–0.964	$k_x\ [DEA]^x$	-	Packed column
Donaldson and Nguyen [17]	25	0.031–0.088	$1400\ [DEA]$ for $[DEA] \to 0$		Facilitated transport in aqueous amine membranes
Groothuis [18]	25	2.0	$1300\ [DEA]$, $830\ [DEA]^*$	-	Stirred cell
Laddha and Danckwerts [30]	25	0.46–2.88	$\frac{[DEA]}{\frac{1}{1410} + \frac{1}{1200[DEA]}}$	-	Stirred cell
Sada et.al.[43]	25	0.249–1.922	$1340\ [DEA]$	-	Laminar jet
Sharma [47] Danckwerts and Sharma [15]	25	1.0	$1500\ [DEA]$, $1240\ [DEA]^*$	41.8	Laminar jet
Sharma [47] Danckwerts and Sharma [15]	35	1.0	$2500\ [DEA]$	41.8	Laminar jet
Leder [32]	80	-	$1.78*10^5[DEA]$	43.9	Stirred cell

*: corrected for $m_{CO_2}\sqrt{D_{CO_2}}$ in table 2

Tertiary alkanolamines do not react directly with CO_2 according to reaction (4), because they lack the free proton. Yet they combine with CO_2 in aqueous solutions by the reactions (5)–(7).

In principle, each of the reactions (4)–(7) for primary and secondary and (5)–(7) for tertiary alkanolamines, contributes to the measured overall reaction rate constant k_{ov}. Some neglections are justified, however. The formation of carbonic acid from CO_2 and H_2O by reaction (6) is very slow ($k = 0.026\ sec^{-1}$ at 25°C[38]) compared to the reactions (4) and (5) at pH > 9.5 as will be shown later. Hence reaction (6) is not incorporated in k_{ov}. By using the data of Jensen *et al.*[22] and Jørgensen[26], it can be calculated that the alkylcarbonate reaction (7) contributes negligibly to the CO_2 absorption rate for MEA[48] and DEA at pH < 12. As this condition is amply fulfilled in our experiments, we neglected this reaction for DEA as well as for DIPA.

On the other hand, the contribution of the bicarbonate formation reaction (5) to the absorption rate can be substantial at low concentrations of secondary amines and is essential for tertiary amines, as will be demonstrated further. This reaction is well documented, e.g. by Pinsent *et al.*[8], and its forward rate constant is expressed by:

$$\log_{10} k^*_{OH^-} = 13.635 - \frac{2895}{T} \text{ (l./mole.sec).} \tag{8}$$

Table 5. Literature data on the reaction between CO_2 and aqueous DIPA

reference	temperature ^oC	[DIPA] mole/l	k_2 l/mole.s	E_{act} kJ/mole	Experimental technique
Sharma [47] Danckwerts and Sharma [15]	15	1.0	230	~ 41.8	Laminar jet
Groothuis [18]	25	2.0	450 550*	-	Stirred cell
Sharma [47] Danckwerts and Sharma [15]	25	1.0	400 440*	~ 41.8	Laminar jet
Sharma [47] Danckwerts and Sharma [15]	35	1.0	680	~ 41.8	Laminar jet

*: corrected for m_{CO_2} $\sqrt{D_{CO_2}}$ in table 2.

Table 6. Literature data on the reaction between CO_2 and aqueous TEA and MDEA

amine	reference	temperature (range) ^oC	[Am mole/l	$k_1 = \frac{r}{CO_2}$ s^{-1}	E_{act} $\frac{kJ}{mole}$	Experimental technique
TEA	Hikita et.al. [19]	20-40	0.0052-0.0078	$10^{(10.72 - \frac{2688}{T})}$ [TEA]	51.5	Rapid mixing method
TEA	Jørgensen and Faurholt [25]	0	0.1, 0.2, 0.5	5930 [TEA][OH^-] [16]	-	Competitive reaction with 0.1 M NaOH
TEA	Jørgensen [26]	18	0.2, 0.4	12730 [TEA][OH^-] [16]	-	Competitive reaction with 0.2 M NaOH
TEA	Barth et.al.[4]	25	0.02 - 0.2	2.85*[TEA]	-	Stopped flow method
TEA	Donaldson and Nguyen [17]	25	0.1 - 1.0	2.7 [TEA]	-	Facilitated transport in aqueous TEA membranes
TEA	Sada et.al. [43]	25	0.50 - 1.60	16.8 [TEA]	-	Wetted wall column
MDEA	Barth et.al. 4	25	0.02 - 0.2	not conclusive	-	Stopped flow method

In our mechanistic model we assume that the carbamate formation from primary and secondary alkanolamines by reaction (4) takes place in accordance with the approach given by Danckwerts[16], derived from Caplow's work[10]. The reaction steps successively involve the formation of a "zwitterion":

$$CO_2 + R_1R_2NH \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} R_1R_2NH^+COO^- \quad (9)$$

and the subsequent removal of the proton by a base B (base catalysis):

$$R_1R_2NH^+COO^- + B \xrightarrow{k_b} R_1R_2NCOO^- + BH^+. \quad (10)$$

For this mechanism Danckwerts[16] derived the forward reaction rate equation at quasi-steady state:

$$r_{(4)} = \frac{k_2[CO_2][R_1R_2NH]}{1 + \frac{k_{-1}}{\Sigma k_b[B]}} \text{(mole/l.sec)} \quad (11)$$

where $\Sigma k_b[B]$ indicates the contribution to the proton removal step (10) by all bases present in the solution.

In a recent second publication on this subject, Laddha and Danckwerts[30] considered only the amine as a base in eqn (11), neglecting contributions by H_2O and OH^-. In several articles[1, 2, 10, 22, 25, 26] these species are shown to have a pronounced effect on the rate of reaction (4). In our model we considered, therefore, incorporation of H_2O and OH^- as bases in (11) to be essential. Rate equation (11) then becomes:

$$r_{(4)} = \frac{k_2[CO_2][R_1R_2NH]}{1 + \dfrac{k_{-1}}{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{R_1R_2NH}[R_1R_2NH]}} \quad \text{(mole/l.sec)} \tag{12}$$

As mentioned before, the overall reaction rate constant k_{ov} covers the contributions by reactions (4) and (5) and can be written as:

$$k_{ov} = k^*_{OH^-}[OH^-] + \frac{k_2 \cdot [R_1R_2NH]}{1 + \dfrac{k_{-1}}{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{R_1R_2NH}[R_1R_2NH]}} \ (\text{sec}^{-1}). \tag{13}$$

For MEA $k_{-1}/(\Sigma k_b[B]) \ll 1$ (as pointed out by Danckwerts[16]), which means that the zwitterion is deprotonated relatively fast in comparison to the reversion rate to CO_2 and MEA and, therefore a simple second order kinetics for reaction (4) results:

$$r_{(4)} = k_2[CO_2][R_1R_2NH] \ \text{(mole/l.sec)} \tag{14}$$

This rate equation thus derived, is independent of hydroxyl ion concentration, which fact is confirmed by the experiments of Jensen *et al.*[22].

Some CO_2-absorption experiments for non-aqueous MEA solutions (MEA–ethanol and MEA–ethylene glycol) have been published very recently by Alvarez-Fuster *et al.*[2]. They found a second order dependence of the reaction rate on MEA concentration. This dependence can be covered by the proposed mechanism because $\Sigma k_b[B]$ is reduced to $k_{R_1R_1NH}[R_1R_2NH]$ and, therefore, probably

$$\frac{k_{-1}}{k_{R_1R_2NH}[R_1R_2NH]}$$

exceeds 1, resulting in an overall third order kinetics:

$$r_{(4)} = \frac{k_2 k_{R_1R_2NH}}{k_{-1}}[CO_2][R_1R_2NH]^2 \ \text{(mole/l.sec)}. \tag{15}$$

The kinetics and mechanism of DEA, DIPA, TEA and MDEA–CO_2 reactions will be discussed together with our experimental results.

EXPERIMENTAL

Independently of Laddha and Danckwerts[30] we developed an almost identical experimental set-up. The basic ideas and the mathematical description are summarized below.

In our experiments we measured the pressure decrease with time due to absorption of pure CO_2 at reduced absolute pressure in using a closed stirred cell reactor. The reaction kinetics were obtained in the pseudo first order reaction regime where the following conditions are satisfied:

$$2 < \text{Ha} \ll E_i \tag{16}$$

with:

$$\text{Ha} = \frac{\sqrt{k_{ov} \cdot D_{CO_2}}}{k_1} \tag{17}$$

and:

$$E_i = \sqrt{\frac{D_{CO_2}}{D_{Am}}} + \sqrt{\frac{D_{Am}}{D_{CO_2}}} \cdot \frac{[\text{Am}] \cdot R \cdot T}{\nu_{CO_2} \cdot P_{CO_2} \cdot m_{CO_2}}. \tag{18}$$

The CO_2-absorption rate is then described by:

$$J_{CO_2} \cdot A = \sqrt{k_{ov} \cdot D_{CO_2}} \cdot m_{CO_2} \cdot \frac{P_{CO_2}}{R \cdot T} \cdot A. \tag{19}$$

In our closed reactor with a gas volume V_g, the pressure-time relation can easily be obtained from an instationary mass balance and becomes:

$$\ln P_{CO_2}|_t = -\frac{m_{CO_2} \cdot A}{V_g} \cdot \sqrt{k_{ov} \cdot D_{CO_2}} \cdot t + \ln P_{CO_2}|_{t=0}. \tag{20}$$

The overall-reaction rate constant, k_{ov}, was determined from the slope in a ln P_{CO_2}-time plot in the region where condition (16) was met.

The apparent reaction rate constant for the carbamate formation reaction (4), k_{app}, is calculated from the overall rate constant k_{ov} by correction for the contribution of the bicarbonate formation by reaction (5):

$$k_{APP} = k_{ov} - k^*_{OH^-}[OH^-] = \frac{k_2[R_1R_2NH]}{1 + \dfrac{k_{-1}}{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{R_1R_2NH}[R_1R_2NH]}} \ (\text{sec}^{-1}). \tag{21}$$

The experimental set-up is shown in Fig. 4. The absorption experiments were carried out in a ~10 cm i.d. all glass, thermostatted stirred-cell reactor at 25.0°C (see Fig. 5). The reactor consists of upper and lower parts which seal on ground flanges. The glass stirrer is equiped with molten in magnets and is driven externally at 60 rpm. The absolute pressure in the reactor is recorded by a mercury pressure indicator and is read by a kathetometer to an accuracy of ~0.02 mm Hg.

Before the experiments the freshly prepared solutions were degassed under vacuum in a separate glass vessel to strip off all inert gas contaminants. After degassing, the solution was fed under vacuum into the stirred-cell reactor and the vapour-liquid equilibrium was allowed to establish. The pressure was read and this value, P_{H_2O}, was used to calculate the actual P_{CO_2} used in eqn (20) from the measured total pressure P_{tot} by:

$$P_{CO_2} = P_{tot} - P_{H_2O}. \tag{22}$$

The P_{H_2O} measured proved to be proportional to the

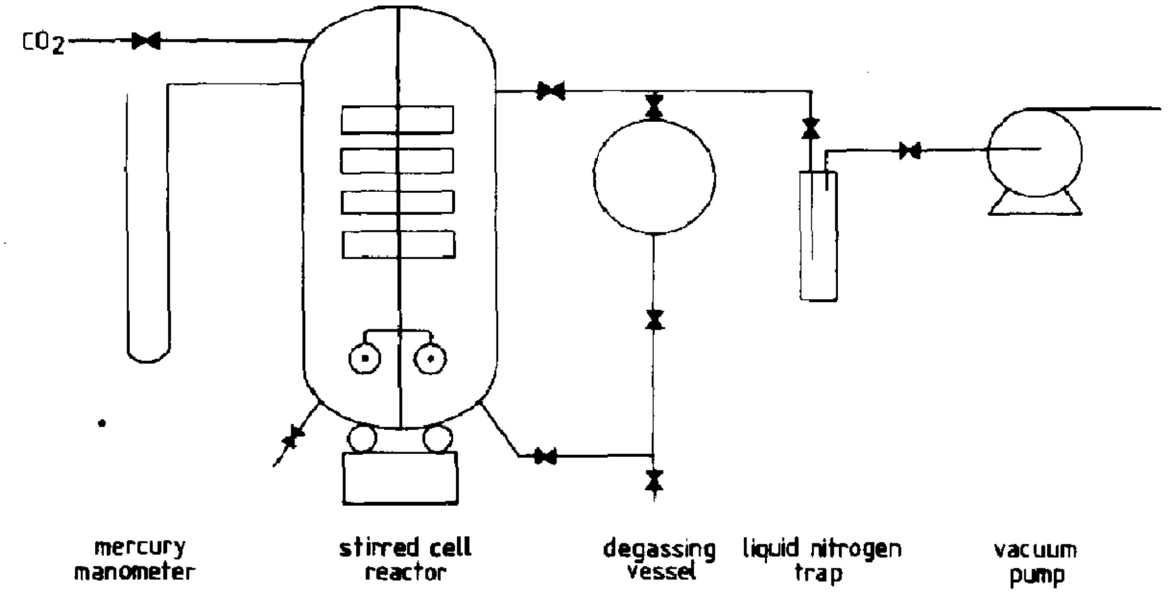


Fig. 4.

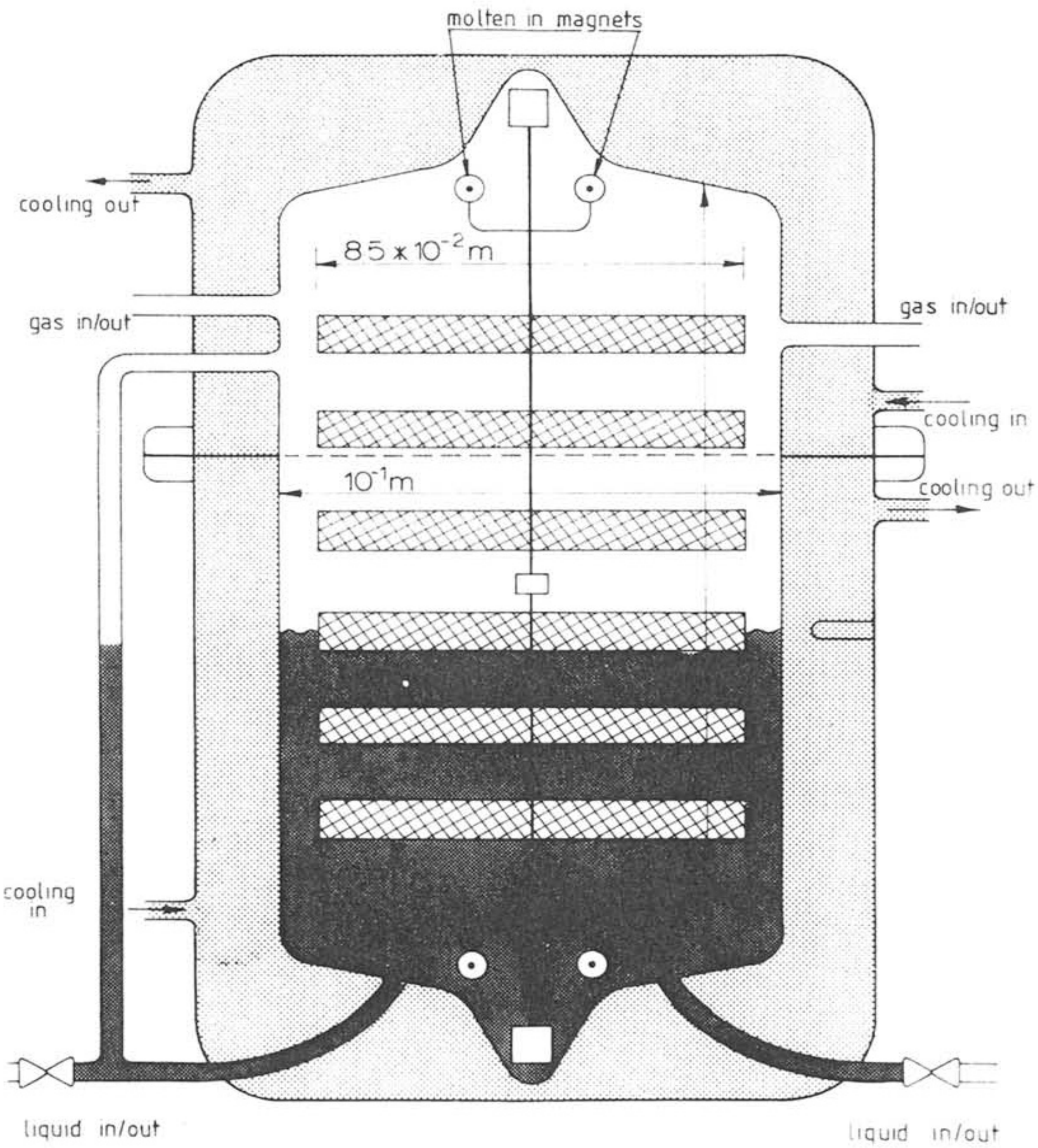


Fig. 5.

mole fraction water at all amine concentrations, according to Raoult's law.

After equilibration, pure CO_2 was introduced into the reactor. By means of the amount of CO_2 both initial pressure $P_{CO_2}|_{t=0}$ and the average CO_2-liquid load for the experiments could be adjusted. By this substantial CO_2 liquid-load primary (and secondary) amine contaminants, if present, were substantially converted to carbamates and their effects on the measured absorption rate could be strongly reduced. On the other hand, the average $[OH^-]$ during the experiments could be adjusted by variation of the liquid-load.

The decrease of P_{CO_2} during the experiment caused E_i to increase steadily (see eqn 18) and, therefore, condition (16) could always be met in part of the pressure-time curve, even if a high initial P_{CO_2} was used to obtain a substantial average CO_2 liquid-load (see Fig. 6 for a typical example). At least 10 pressure-time readings in the region where condition (16) was met were used to obtain the overall reaction rate constant k_{ov}. Duplicate runs varied only 3% in k_{ov} at the maximum.

After the experiment, the solution was analysed for total amine by standard potentiometric titration with 0.500 M hydrochloric acid and for total CO_2 by the method described by Verbrugge[49] and Jones et al.[24]. From this final CO_2 content and the pressure-time readings an average CO_2 liquid-load during each experiment was calculated. The equilibrium model described by Blauwhoff and van Swaaij[6] was used for calculation of hydroxyl ion and actual free amine concentrations from average CO_2 liquid load and total amine concentration. This model includes, among others, equilibrium reactions (4)–(6), and the carbamate hydrolysis equilibrium. At the relatively low CO_2 loadings in our investigations the effect of this latter equilibrium on the amount of the actual free amine concentration used for the calculations is, however, generally negligible.

The influence of the CO_2 liquid-loading in the experiments on the rate of the reverse of reaction (4) and with that its effect on the measured absorption flux J_{CO_2} was checked for DIPA using the numerical solution technique described by Cornelisse et al.[14]. For this check, calculated molefluxes with and without CO_2 liquid-loads in the experimental range, having the same real free amine bulk concentrations (obtained with the equilibrium model) were compared. The difference in molefluxes amounted to 1% at the maximum for the combination of the lowest DIPA concentration and the highest CO_2 liquid-load. The effect of the reversibility on measured reaction rate constants could, therefore, be neglected.

RESULTS

DEA and DIPA

For both DEA and DIPA, three series of CO_2 absorption experiments (A, B and C) were carried out at 25°C. A range of amine concentrations was applied within each series (see Tables 7 (DEA) and 8 (DIPA)).

In the A- and B-series in almost constant average CO_2

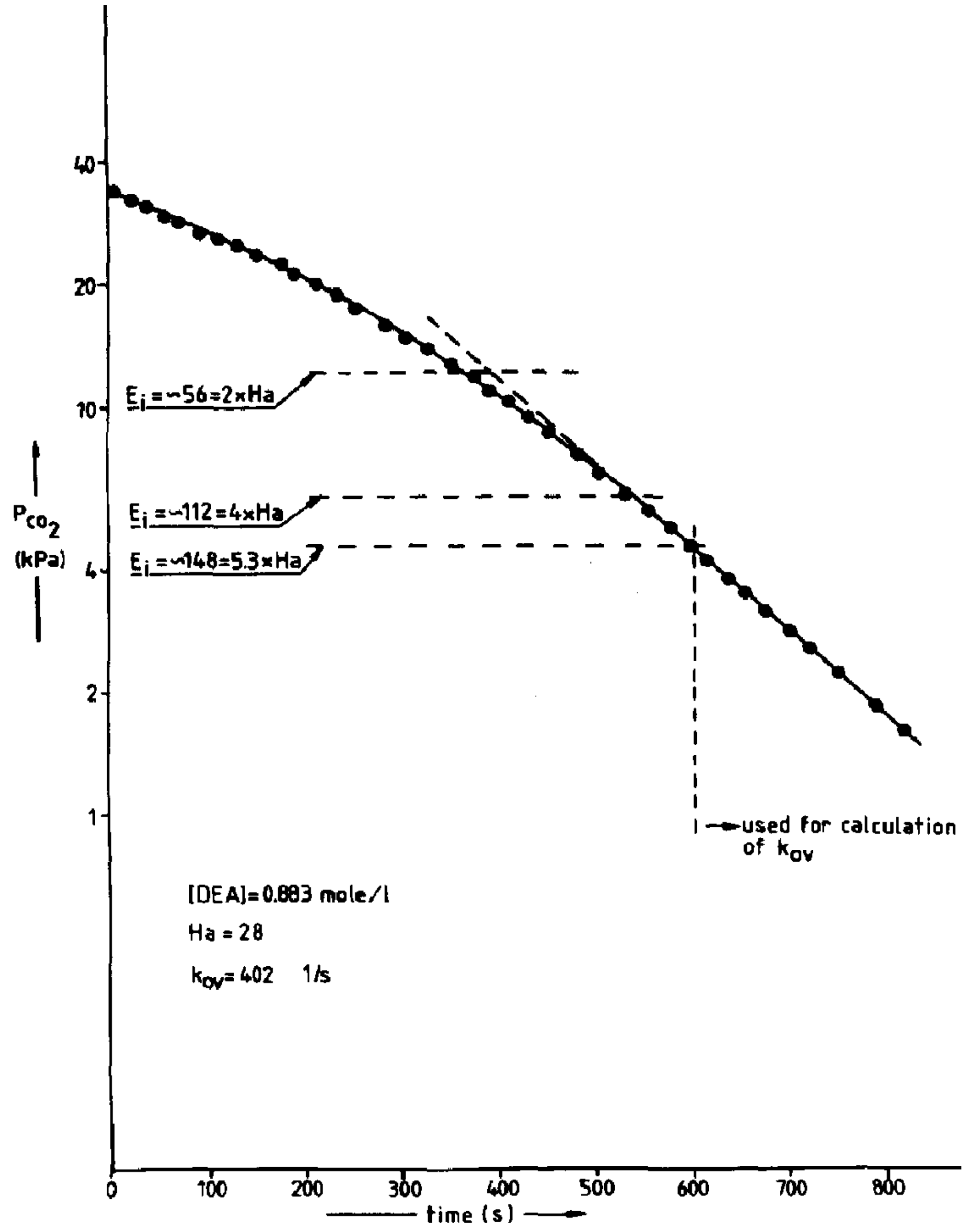


Fig. 6.

Table 7. Experimental results for DEA at 25°C (present investigation)

	[DEA] mole/l	$[CO_2]_l^{tot} * 10^2$ mole/l	$[OH^-]*10^4$ mole/l	$[H_2O]$ mole/l	k_{app} s^{-1}
A	0.509	1.19	3.15	52.6	199.5
	0.516	1.15	3.33	52.6	213.1
	0.900	1.15	5.67	50.6	466.0
	0.980	1.29	5.68	50.1	512.9
	1.978	0.74	15.28	45.0	1416
	2.031	0.69	16.20	44.7	1488
	2.045	0.66	17.04	44.7	1575
B	0.883	4.28	1.97	50.4	400.4
	1.374	3.78	3.34	47.8	758.2
	1.731	3.99	4.03	45.9	1030
	1.874	3.80	4.28	45.3	1178
	1.953	4.26	4.36	44.8	1250
C	0.393	4.02	0.93	53.0	132.7
	0.586	4.03	1.38	51.9	220.1
	0.766	3.87	1.85	51.0	308.3
	1.665	2.37	5.79	46.5	1146
	1.834	9.68	2.20	44.9	1060
	1.834	9.51	2.23	44.9	1090
	1.881	6.64	2.99	44.9	1131
	1.883	7.45	2.74	44.8	1130
	1.889	1.42	9.84	45.4	1423
	1.956	3.97	4.56	44.8	1150
	2.033	0.76	15.60	44.7	1448
	2.164	1.21	12.00	44.0	1548
	2.169	1.33	11.50	44.0	1545
	2.308	2.59	7.44	43.1	1760

liquid concentration was realized in the way previously described. The measured apparent rate constants have been plotted logarithmically versus $\ln[R_1R_2NH]$ in Fig. 7. Two important features can be observed: (1) the apparent reaction order in amine, n_{app}, is ~1.3 increasing with amine concentration to ~1.5 for DEA and ~1.6 to ~1.8 for DIPA; (2) the apparent rate constant decreases with rising CO_2 liquid-load.

The first point confirms that the reaction mechanism is not simple and straightforward indeed, and indicates that more complicated schemes, like the one proposed in this paper, are needed to explain the results.

The second point can be explained only by a decrease of the hydroxyl ion concentration with increasing CO_2 liquid load because its influence on real free amine concentration, $[R_1R_2NH]$, is incorporated using the equilibrium model mentioned earlier[6]. This effect is in line with the mechanism proposed and the reaction rate equation (12) derived. In the experiments by Laddha and Danckwerts[30], however, the average CO_2 liquid-load was not varied systematically, as can be concluded from their experimental description. Hence this influence could probably not be discerned and was consequently not incorporated in their reaction rate equation.

We analysed the proposed reaction mechanism by fitting k_{app} (eqn 21) to all our experimental results, minimizing the sum of least squares by a linear regression technique. In this way we determined the values of

$$k_2, \frac{k_2 k_{H_2O}}{k_{-1}}, \frac{k_2 k_{OH^-}}{k_{-1}} \text{ and } \frac{k_2 k_{R_1R_2NH}}{k_{-1}}$$

(see Table 9). The average deviation between the experiments and the fitted model is extremely small.

Some very important conclusions can be drawn from the results in Table 9, which hold both for DEA and DIPA: firstly, $1/k_2$ is less than 10% of

$$\frac{k_{-1}}{\Sigma k_b[B]}$$

at all amine concentrations. For this reason, the exact

Table 8. Experimental results for DIPA at 25°C (present investigation)

	[DIPA] mole/l	$[CO_2]_l^{tot} * 10^2$ mole/l	$[OH^-] * 10^4$ mole/l	$[H_2O]$ mole/l	k_{app} s^{-1}
A	0.334	0.66	3.09	53.0	34.4
	0.334	0.65	2.96	53.0	32.7
	0.466	0.76	4.21	52.1	60.4
	0.470	0.64	4.25	52.1	65.2
	0.494	0.74	4.45	51.9	63.4
	1.056	0.73	8.99	48.0	226.5
	1.061	0.72	9.03	47.9	231.9
	1.063	0.74	9.03	47.9	232.4
	1.981	0.73	15.80	41.6	771.7
	1.985	0.78	15.80	41.5	771.5
	2.143	0.66	19.30	40.5	837.7
	2.887	0.76	21.90	35.3	1490
	2.905	0.76	22.00	35.2	1513
B	0.534	3.77	1.33	51.2	63.1
	0.541	4.08	1.27	51.0	62.8
	0.990	3.41	2.63	48.1	182.0
	1.008	3.88	2.42	47.9	195.8
	1.046	3.60	2.65	47.7	213.1
	1.814	3.25	4.95	42.4	515.1
	1.836	3.22	5.04	42.2	550.0
	2.612	3.68	6.44	36.8	1059
	2.658	3.77	6.44	36.5	1075
C	0.931	5.24	1.78	48.3	168.9
	0.987	2.52	3.32	48.2	187.5
	0.992	2.54	3.31	48.2	173.9
	1.274	0.64	12.70	46.4	326.8
	1.517	0.73	12.50	44.8	415.1
	1.575	0.75	12.90	44.4	444.7
	2.095	4.74	4.27	40.9	684.4
	2.157	1.97	8.57	40.4	765.3

values of k_2 could not be determined, but the minimum values seem to be $\sim 5 \times 10^3$ l/mole.sec, which is in the same order of magnitude as the rate constant for the CO_2–MEA reaction. This implies that the rates of formation of the zwitterions for DEA and DIPA are at least in the same range as for MEA.

Secondly, it follows:

$$\frac{k_{-1}}{\Sigma k_b[B]} \gg 1 \tag{23}$$

indicating that the larger part of the zwitterions is reverted to CO_2 and amine and that only a small part is converted to carbamate. This limited stability is the essential difference with the CO_2–MEA reaction. Using (23), rate eqn (12) can be simplified to:

$$r_{(4)} = \frac{k_2}{k_{-1}}[CO_2][R_1R_2NH] \times \{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{R_1R_2NH}[R_1R_2NH]\} \quad \text{(mole/l.sec)}. \tag{24}$$

This rate equation is basically different from the one used by Laddha and Danckwerts[30]:

$$r_{(4)} = \frac{[CO_2][R_1R_2NH]}{\dfrac{1}{1410} + \dfrac{1}{1200[R_1R_2NH]}} \quad \text{(mole/l.sec)}. \tag{25}$$

At very low amine concentrations, condition (23) is fulfilled and our rate equation (24) tends to a first order dependency of $r_{(4)}$ in amine, $k_{H_2O}[H_2O]$ becoming the

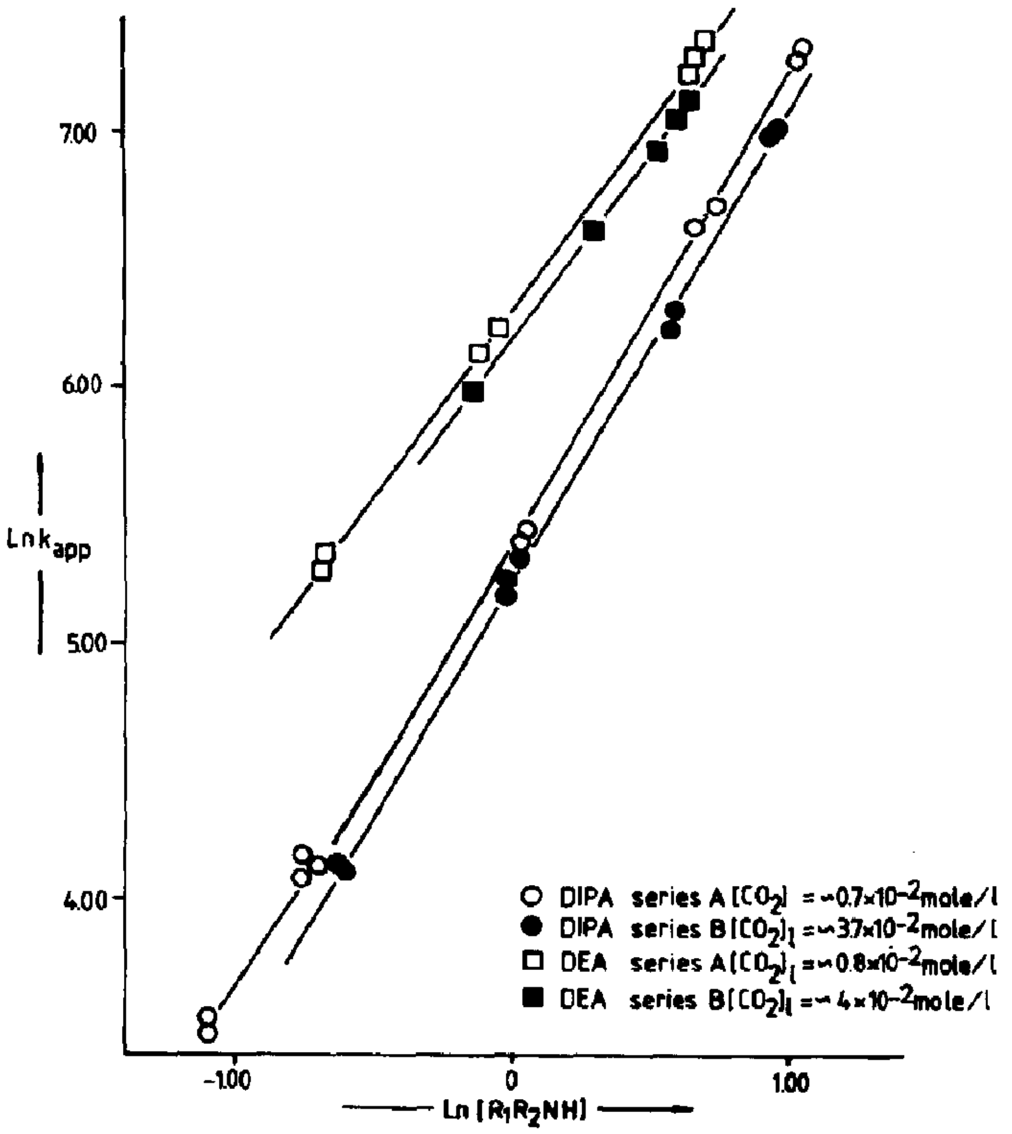


Fig. 7.

Table 9. Fitted values of kinetic constants $k_2, \frac{k_2 k_{H_2O}}{k_{-1}}, \frac{k_2 k_{OH^-}}{k_{-1}}$ and $\frac{k_2 k_{R_1R_2NH}}{k_{-1}}$ for DEA and DIPA at 25°C

	k_2 1/mole.s	$\frac{k_2 k_{H_2O}}{k_{-1}}$ $l^2/mole^2.s$	$\frac{k_2 k_{OH^-}}{k_{-1}}$ $l^2/mole^2.s$	$\frac{k_2 k_{R_1R_2NH}}{k_{-1}}$ $l^2/mole^2.s$	average deviation %
DEA	> 5800	5.34	$7.05 * 10^4$	228	3.3
DIPA	> 5300	0.813	$4.17 * 10^4$	144.6	3.4

governing factor. Equation (25) by Laddha and Danckwerts[30], however, tends to a second order dependency in amine. Our eqn (24) agrees, therefore, with the trend found by the British Gas Corp. (mentioned by Laddha and Danckwerts[30]). On the other hand, a second order in amine is predicted by eqn (24) at high amine concentrations, provided conditions (23) is still met, which is in agreement with Nunge and Gill[34]. Rate expression (25) of Laddha and Danckwerts predicts in this case a first order in amine.

Thirdly, comparing the relative magnitudes of the "partial rate constants",

$$\frac{k_2 k_{H_2O}}{k_{-1}}, \frac{k_2 k_{OH^-}}{k_{-1}} \text{ and } \frac{k_2 k_{R_1R_2NH}}{k_{-1}}$$

(Table 9) an increase is found with increasing basicity of the base in the proton removal step (10). This Brønsted effect is clearly shown in Fig. 8 (DEA: $pK_a = 8.88$ at 25°C[37]; DIPA: $pK_a = 8.88$ at 25°C[7]). It is also significant that the "partial rate constants" for DEA are larger than for DIPA, most likely caused by the larger

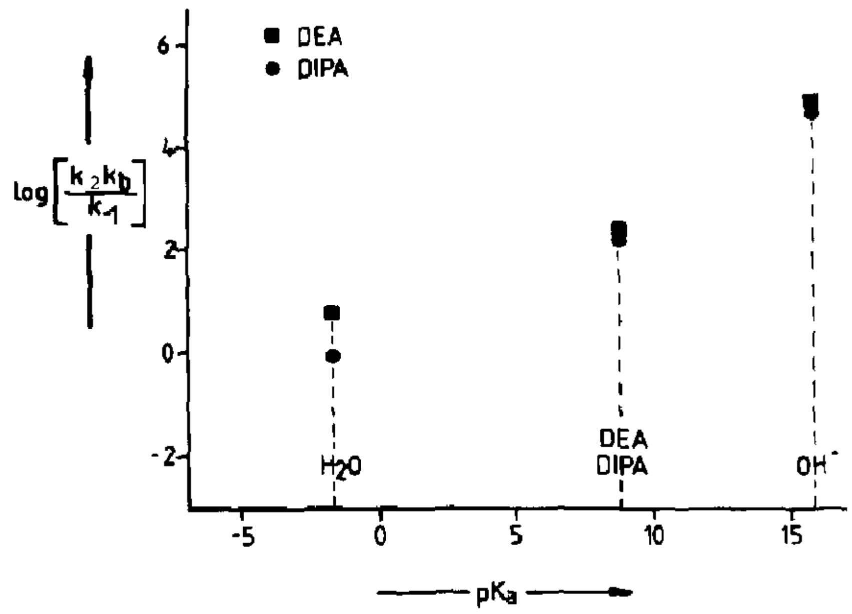


Fig. 8.

steric hindrance for DIPA in the base-catalysed proton removal step (10).

In Figs. 9 and 10 our fitted rate equation lines for the *A*- and *B*-series of DEA and DIPA are shown together with literature data from Tables 4 and 5 at 25°C and our rate constant equation (21), extrapolated to a zero CO_2 liquid-load.

To DEA the following remarks apply. Neither the data of Sada *et al.*[43], nor those of Hikita *et al.*[19] and Sharma[47] agree well with our apparent rate constants and all data exceed our measurements, as well as those of Laddha and Danckwerts, significantly. The reason for these discrepancies cannot be derived from the original articles but might be caused by primary amine contaminants. On the other hand, Groothuis'[18] single data point coincides with our value at zero CO_2 liquid load. Laddha and Danckwerts' measurements[30] fall between our line calculated for zero CO_2 liquid-load and the experimental one for an average ~0.010 moles/l.CO_2 load. This might indicate a small and varying CO_2 load in their experiments, but this was not specified in their work. The rate expression by Blanc and Demarais[5] agrees fairly well with the results in our experimental concentration range (0.39 < [DEA] < 2.3 mole/l.), although their reaction order in DEA is lower (= 1) and constant. Part of this effect may be attributed to the varying CO_2 liquid load along their wetted-wall column. This affects the hydroxyl ion concentration at the different DEA concentrations in a systematic way and hence the bicarbonate reaction (5) contributes differently for each amine concentration to the overall absorption rate. This reaction (5) has a large influence on the overall reaction rate at low amine concentrations. In Fig. 11 the results of Blanc[5], corrected for reaction (5), are compared with the calculated values of our model.

A very strong support for our mechanism was obtained by extrapolating the work on DEA of Jørgensen[26] at 0°C and Jensen *et al.*[22] at 18 to 25°C. In their experiments a high pH was realized by the addition 0.1–0.3 M NaOH. Our calculations by rate equation (21) and their extrapolated measurements are shown in Table 10 and agree well if the extrapolation of (21) over ~3 pH units is taken into account. This agreement cannot be achieved by any other rate expression given in literature (e.g. [19, 30]) as these do not incorporate the effect of $[OH^-]$ on the reaction rate.

For DIPA both Sharma's [47] and Groothuis' [18] results are relatively high, possibly due to contamination by primary amines as mentioned earlier.

TEA and MDEA

Also for TEA and MDEA, absorption experiments were carried out at 25°C with different amine concentrations and CO_2 liquid loads (see Tables 11 and 12 and Fig. 12).

Due to the absorption of CO_2 the hydroxyl ion concentration decreased continuously during an experiment and with that the contribution of the bicarbonate reaction (5) to the absorption rate decreased significantly. The resulting ln P_{CO_2}-time plot, therefore, did not show a linear relation as predicted by eqn (20) because of the declining k_{ov}. This problem was overcome by calculating k_{ov} for each interval between two pressure-time readings and individual correction of this k_{ov} for the bicarbonate reaction (5) by eqn (21) to obtain an instantaneous k_{app}. These apparent rate constants did not vary over a large pressure range and hence were independent of CO_2 liquid load and $[OH^-]$.

Had monoalkylcarbonate formation (7) been one of the prevailing reactions, an influence of $[OH^-]$ would have been expected during the experiments. Using the third order rate constant for this reaction with TEA as extrapolated by Donaldson and Nguyen[17] ($k_3 = 1.53 \times 10^4$ $l^2/mole^2 sec$) from the experiments of Jørgensen and Faurholt[25] and Jørgensen[26], the contribution of this reaction during absorption would have decreased from ~1 to ~0.2 sec^{-1} during some of our experiments. This pseudo first order rate constant is in the same range as the measured ones and the decrease would have been observed if this occurred.

Based on our measured results, therefore, we conclude that no or negligible monoalkylcarbonate formation had taken place. As an independent check we carried out experiments similar to those of Chan and Danckwerts[11] but no substantial reaction products of CO_2 and TEA, e.g. monoalkylcarbonate were detected.

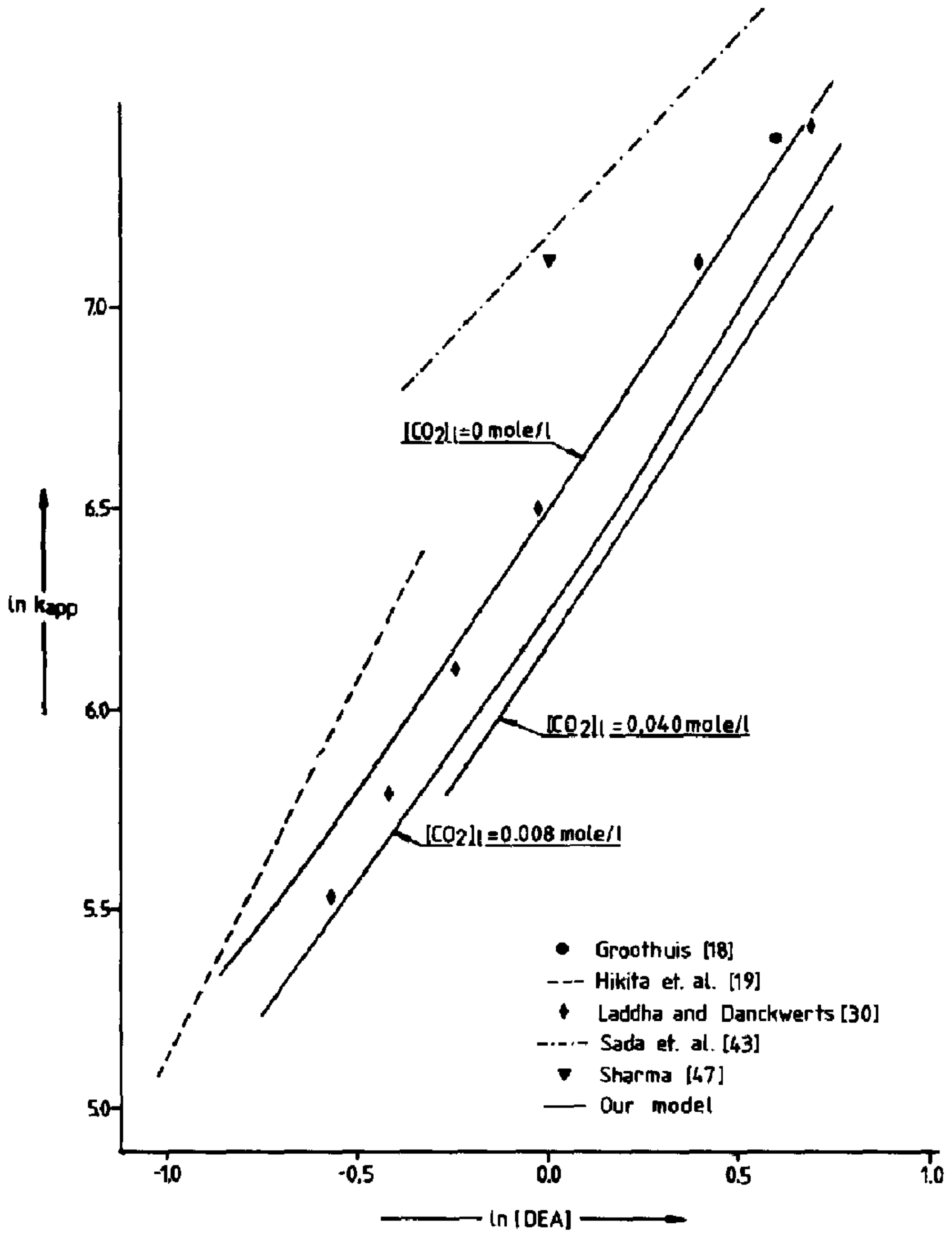
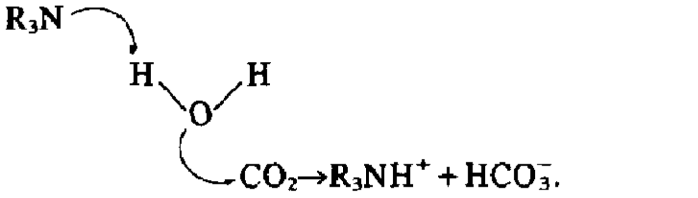


Fig. 9.

The only way to explain the phenomena described above is by a base catalysis of the CO_2 hydratation reaction (6) as proposed by Donaldson and Nguyen[17]. The essence of this catalysis is assumed to be a hydrogen bonding between the real free amine and water which increases the reactivity of water towards CO_2:



(26)

The reaction rate constants measured are $k_2 = 2.9$ l./mole.sec for TEA and $k_2 = 4.8$ l./mole.sec for MDEA respectively.

Comparing these rate constants together with the pK_a's of TEA ($pK_a = 7.76$ at 25°C[37]) and MDEA ($pK_a = 8.52$ at 25°C[37]) a positive effect of amine basicity on catalytic activity is observed. As the pK_a values of TEA and MDEA are lower than the actual solution pH (>9.5), the larger part of the amine is not protonated and therefore catalytically active. Donaldson and Nguyen[17] showed experimental results with triethylamine which they observed to have a negligible catalytic activity on reaction (26). The reason for this is the high pK_a of triethylamine ($pK_a = 10.75$ at 25°C[37]) which in their solution of pH ~ 9.5 results in a very low concentration of catalytically active unprotonated triethylamine.

Our rate constant measured for TEA corresponds very well with the result obtained by Donaldson and Nguyen[17] ($k_2 = 2.0-2.8$ l./mole.sec) and Barth *et al.*[4] ($k_2 = 2.85$ l./mole.sec). Compared to Hikita *et al.*[19] ($k_2 = 50.1$ l./mole.sec at 25°C) and to Sada *et al.*[43] ($k_2 = 16.8$ l./mole.sec at 25°C) our results and those of Donaldson and Nguyen are substantially lower. As for DEA and DIPA the reason for this very large difference can not be made clear from their articles but possibly originates from primary and secondary amine contaminants which accelerate the CO_2 absorption rate. In Donaldson and Nguyen, Barth *et al.*'s[4] and in our experiments this problem is avoided or at least reduced

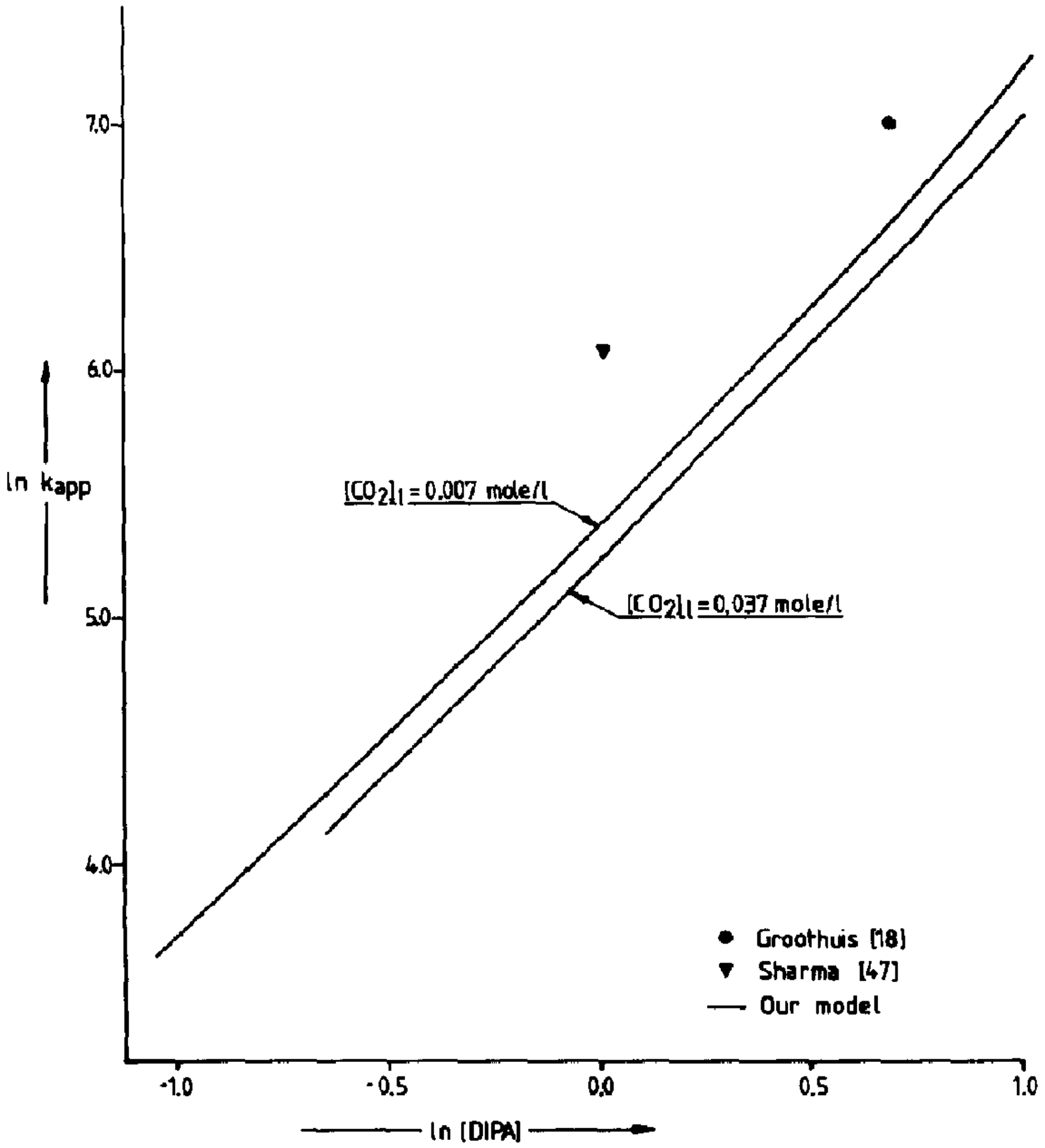

7.0
6.0
5.0
4.0
ln kapp
[CO2]l = 0,007 mole/l
[CO2]l = 0,037 mole/l
Groothuis [18]
Sharma [47]
Our model
-1.0
-0.5
0.0
0.5
1.0
ln [DIPA]

Fig. 10.

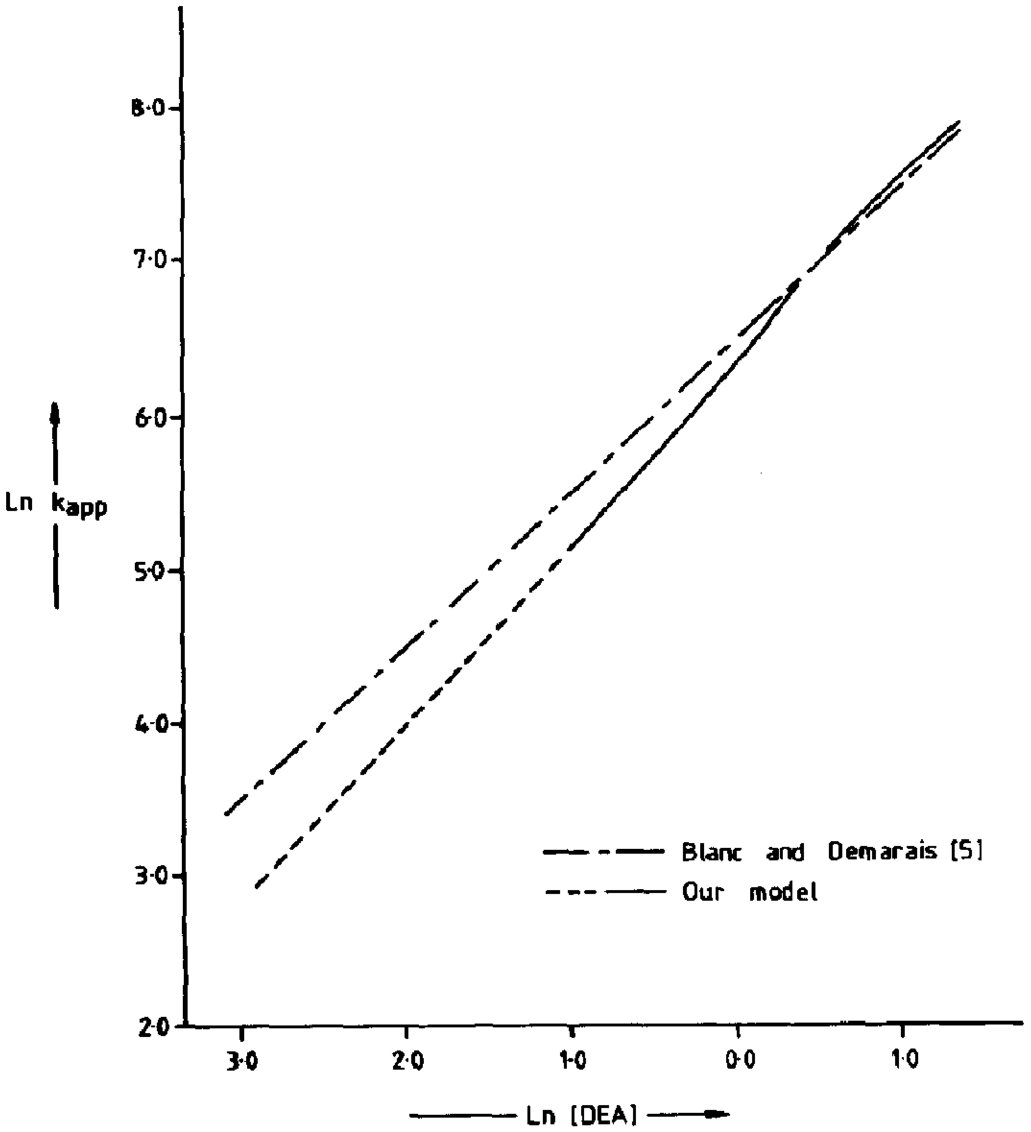

8·0
7·0
6·0
5·0
4·0
3·0
2·0
Ln kapp
Blanc and Demarais [5]
Our model
3·0
2·0
1·0
0·0
1·0
Ln [DEA]

Fig. 11.

Table 10. Comparison of our kinetic model with reaction rate constants extrapolated from Jørgensen[26] and Jensen *et al.*[22]

initial concentrations		Jørgensen [26] 0^oC			Jensen et.al. [22] 18^o			extrapolation 25^oC	our model 25^oC
		average concentrations calculated [16]			average concentrations calculated [16]				
$[OH^-]$ mole/l	[DEA] mole/l	$[OH^-]$ mole/l	[DEA] mole/l	k_2 1/mole.s	$[OH^-]$ mole/l	[DEA] mole/l	k_2 1/mole.s	k_2 1/mole.s	k_2 1/mole.s
0.1	0.1	0.0859	0.0949	1155	0.0876	0.0957	5070	8590	4050
0.2	0.1	0.1837	0.0958	1630	0.1810	0.0959	5430	8340	5830
0.1	0.2	0.0874	0.1931	1165	0.0888	0.1944	4730	7790	4100

Table 11. Experimental results for TEA at 25°C (present investigation)

[TEA] mole/l	$[CO_2]_l$ start mole/l	$[CO_2]_l$ end mole/l	$[OH^-]$ $*10^5$ start mole/l	$[OH^-]$ $*10^5$ end mole/l	k_{app} s^{-1}
0.523	0.0020	0.0114	11.3	2.8	1.34
0.524	0.0019	0.0074	11.8	4.0	1.35
0.667	0.0026	0.0114	11.4	3.5	1.96
0.684	0.0016	0.0097	16.7	4.0	1.69
0.963	0.0026	0.0098	15.5	5.4	2.87
1.314	0.0023	0.0085	22.0	8.0	4.09
1.435	0.0013	0.0218	28.5	4.1	4.16
1.874	0.0905	0.110	1.8	1.5	5.21
1.891	0.0837	0.105	1.9	1.6	5.64

Table 12. Experimental results for MDEA at 25°C (present investigation)

MDEA mole/l	$[CO_2]_l$ start mole/l	$[CO_2]_l$ end mole/l	$[OH^-]$ $*10^5$ start mole/l	$[OH^-]$ $*10^5$ end mole/l	k_{app} s^{-1}
0.45	0.0079	0.0224	16	6.8	2.1
0.76	0.0076	0.0222	25	11	3.3
1.05	0.0073	0.0225	34	14	4.7
1.14	0.0075	0.0224	36	16	5.4
1.59	0.0074	0.0512	50	11	7.0
1.63	0.0073	0.0162	51	27	8.4

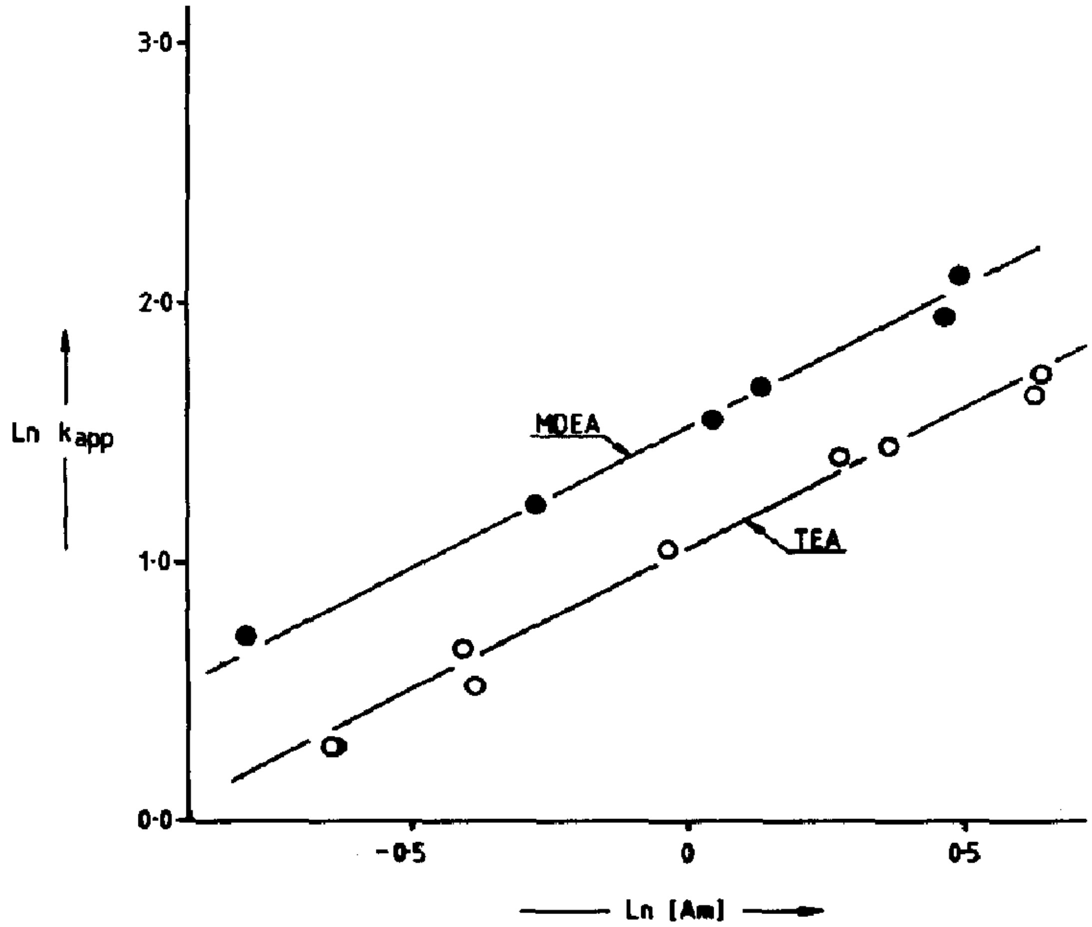


Fig. 12.

by the substantial CO_2 liquid load which "neutralizes" the contaminants.

CONCLUSIONS

The available literature data provide a good basis for the calculation of the rate constant of the CO_2–MEA reaction, which is first order in the amine.

Our data measured on DEA and DIPA are very well described by the rate expression derived from the proposed mechanism. The results of Laddha and Danckwerts[30] agree well with our measurements. In their model, however, they do not incorporate H_2O and OH^- as bases and so arrive at a reaction rate expression which depends only on the amine concentration. Our data showed a significant dependence on $[OH^-]$ and, therefore, we incorporated $[OH^-]$ in our reaction mechanism. The good extrapolation of our model to the high pH measurements of Jørgensen[26] and Jensen *et al.*[22] is a strong support for the proposed mechanism.

With TEA and MDEA, no alkylcarbonate formation was observed. A base catalysis mechanism of the CO_2 hydratation reaction fits the phenomena observed and is in agreement with Donaldson and Nguyen[17].

NOTATION

A interfacial area, m^2
Am amine
B base
D diffusion coefficient, m^2/sec
E_i infinite enhancement factor defined by eqn (18)
Ha Hatta number defined by eqn (17)
J mole flux, mole/m^2sec
k_1 first order reaction rate constant, sec^{-1}
$k-1$ reaction rate constant see eqn (9), sec^{-1}
k_2 reaction rate constant, l./mole.sec
k_{app} apparent rate constant defined by eqn (21), sec^{-1}
k_b, k_{H_2O}, k_{OH^-}, rate constants defined by eqns (11) and (12), l./mole.sec
k_l liquid phase mass transfer coefficient, m/sec
k^*_{OH} reaction rate constant for bicarbonate formation defined by (8), l./mole.sec
k_{ov} overall rate constant defined by (13), sec^{-1}
m dimensionless solubility
n_{app} apparent reaction rate order in amine
P pressure, Pa
$r_{(4)}$ rate of reaction (4), mole/l.sec
R gas constant, l.Pa/mole.°K
t time, sec
V volume, m^3
η viscosity, Pa.sec
ν stoichiometric coefficient

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